

**RECOVERY OF SOME VOLATILE COMPONENTS
FROM MANGO AND GUAVA**

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INTRODUCTION

Research on natural flavor components of foods has expanded rapidly in the past decade. Perhaps the greatest advances have been in studies of natural flavor constituents of fruits. Chemical analysis of these flavors requires the concentration, fractionation, and identification of minute quantities of chemical compounds. Analyses have been reported for several fruits, but the most complete studies have been made on strawberries (2) and on citrus fruit (8, 12). In the latter investigation specific chemical changes of flavor compounds were determined on canned and stored products. It is important that these changes be known in order to develop improved processes for maintaining the natural fresh flavor of fruits.

Many tropical fruits are characterized by especially delicate and aromatic flavor factors. Retention of tropical fruit flavors during processing and storage is difficult to obtain by conventional processing methods. Thus, chemical analyses of the components of flavor and odor of tropical fruits and their juices are important to progress in the development of processed products of this type. Few such analyses are available in the published literature. Ester contents of banana (13) and of pineapple (5) have been reported. The most extensive investigation of the flavor components of a strictly tropical fruit is the work by Hiu (6) on passion fruit (*Passiflora edulis* f. *flavicarpa*, Degener) in Hawaii.

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Hiu recovered from 0.0023 to 0.0043 percent volatile oils from passion fruit juice by flash distillation, fractionation, and extraction. The oil was found to be similar to that in grapefruit juice in which one volatile compound is largely responsible for flavor and odor characteristics. The principal component of the volatile essence of passion fruit was found to be n-hexylcaproate.

The mango (*Mangifera indica*) is well known in tropical regions for its characteristic aroma and distinctive flavor. That its flavor components may not be entirely exotic, however, is indicated by the observation that it sometimes exhibits a flavor considered more peach than peach. Nevertheless, it is also characterized by its distinctive mango flavor, sometimes referred to as "terpeny," depending upon the variety. Another important component of the mango is an allergen, which may or may not be associated with its flavor components. This allergen is considered to be 3-pentadecylcatechol, as has been found in other plants of the mango family (Anacardiaceae), including poison ivy (*Rhus*).

In view of distinctive flavor properties and processing difficulties in retaining these, knowledge of mango flavor components is needed. The present investigation was initiated to provide methods and procedures adaptable to the fruit and to contribute preliminary information on chemical composition of the flavor extractant. The common Haden mango of Hawaii was used. A limited study was also made of the common guava of Hawaii (*Psidium guajava* L.).

RECOVERY OF MANGO ESSENCE

Firm, ripe mangos were peeled and deseeded. The flesh was pureed by hand and pressed through a single thickness of nylon cloth with a hydraulic press. The juice, totaling 106.2 kg. in weight, was diluted with twice its weight of water, and steam-distilled at a rate of 357–420 ml/minute in an essence recovery unit after Walter and Patterson (14) (fig. 1). Although total time for a run was approximately 8 hours, any fermentation initiated during the latter part of the holding period was not considered to have contributed appreciably to the volatile components.

The mango juice was fed continuously from (a) by pump (b) to the preheating tube (c). The juice emerged at a temperature just below boiling into the vaporizer (d), where it was allowed to reach boiling temperature. A mixture of vapor and liquid was ejected through a small orifice (e), at the end of the vaporizer, into the separator (f), where separation between the liquid and vapor took place.

The volatiles emerged from the separator through a fractionating column. Condensation occurred at (h) and the distillate was collected at (i). A slow return of the distillate to the fractionating column was made possible by

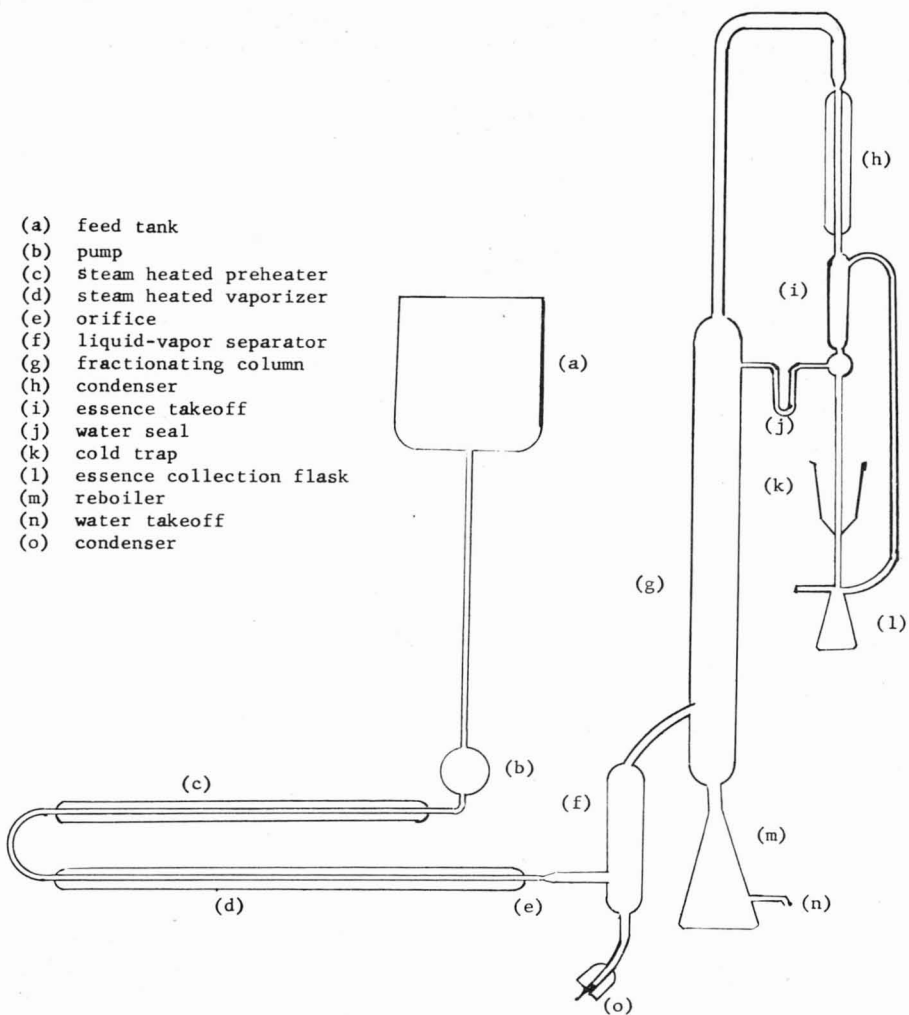


Figure 1. Essence extraction unit.

water seal (j). This system provided for continuously concentrating the distillate. Water fractionated from the system was collected at (m) and was periodically drawn off at (n).

The liquid from the separator passed through a condenser and was collected for a repass through the extraction unit. Periodic tests on the stripped juice showed that much of the mango aroma was lost in a single pass.

Bright yellow drops of oil were visible on a large amount of aqueous distillate. The oil was extracted with petroleum ether, boiling point 35° – 40° C., and the aqueous residue which represented an 80-fold concentration by weight, was fractionated by a Vigreux column. The low boiling portion, up to 85° C., was collected for analyses and represented an approximate 800-fold concentration from the original mango juice. A petroleum ether extract of the still material was made to remove all traces of mango oil. The ether extracts were combined and fractionated to remove the solvent. The residue, approximately 0.5 ml. of yellow oil, appeared to have a very concentrated mango aroma and represented a 1.9 p.p.m. concentration in the fruit.

ANALYSES OF LOW BOILING PHASE

Carbonyl determination

A determination for the total carbonyl content of the low boiling fraction as acetaldehyde was made, using a slight modification of the method of Lappin and Clark (9). Twenty-four and six-tenths mg. of the sample were diluted up to 10 ml. with carbonyl-free ethanol. One ml. of this solution was made to react with 1 ml. of a saturated ethanol solution of 2,4-dinitrophenylhydrazine in the presence of a drop of concentrated hydrochloric acid. The reaction mixture was heated in a water bath maintained at a temperature of 50° C. for 30 minutes. Upon cooling, 5 ml. of an alcoholic potassium hydroxide solution was added. Two ml. of water was added and a reading was made against a suitable blank at $480\text{ m}\mu$ on a Beckman DU spectrophotometer. The reading was compared with a calibration curve for acetaldehyde-2,4-dinitrophenylhydrazone (2,4-DNPH) and was found to correspond to 13.7 p.p.m. of acetaldehyde in the original mango juice.

An attempt was made to identify the carbonyl compounds. A sample of the low boiling fraction of mango distillate was reacted with 2,4-dinitrophenylhydrazine (1), and the precipitated hydrazones were chromatographed on a bentonite-kieselghur column by the method of Elvidge and Whaley (3). Two bands formed on the column, and one was easily eluted with chloroform. The second band required a more polar solvent, and a mixture of 1 part ethanol to 19 parts of chloroform was used. The chloroform eluate was greenish-yellow, but turned brownish-orange as attempts were made to concentrate the solution. Crystallization of the hydrazone did not take place, and only a brown oil was obtained. Further work on this fraction was postponed. The chloroform-methanol eluate proved more amenable to crystallization, and a

small amount of solid was obtained. The melting point of this product was 141°–149° C. The highest melting point that was obtained after two to four more passes through column was 157°–160° C. It was compared with the melting point of acetaldehyde-2,4-DNPH, which is 167° C. (1).

The unknown hydrazone was paper-chromatographed with several known hydrazones, among them, that of acetaldehyde, under two different conditions. The results from the method of Lynn, Steele, and Staple (10), using phenoxylethanol-saturated heptane, showed that the mobility of the unknown after 18 hours was 10 cm—the same as for acetaldehyde, 2,4-DNPH. The R_f value of the unknown using the method of Meigh (11), using methanol-saturated heptane, at 10° C., varied from one chromatograph to another. However, within each one, the R_f value of the unknown was the same as for acetaldehyde-2,4-DNPH.

The results of a few sample paper chromatograms are as follows:

	R_f unknown	R_f acetaldehyde-2,4-DNPH
Trial a	.49	.48
b	.60	.60
c	.60	.60

Results from both methods of paper chromatography were considered to indicate that one of the carbonyl compounds present in mango is acetaldehyde.

Alcohol determination

The method of Holley and Holley (7) was followed for forming the 3,5-dinitrobenzoic acid esters of the alcohols in the low boiling fraction. The benzoates (3,5-DNB's) of known alcohols were spotted on paper (11) and irrigated at 10° C. with methanol-saturated heptane according to Meigh (11). Only one spot appeared from the unknown, and the R_f corresponded to that of ethanol-3,5-DNB.

ANALYSES OF OIL PHASE

Gas Chromatography

A gas chromatogram of the mango oil was made. The sample was allowed to pass through a 10-foot silicone column at a pressure of 42 cm. and at 184° C. Although only one well-defined peak was recorded, the chromatogram showed that the oil was not a pure compound but a mixture of several. It was not possible to determine the number of components from this single chromatogram.

Optical measurements

The infrared spectrum of the oil was obtained, and strong absorption bands in the carbonyl region were observed. A number of weaker bands in the fingerprint region were also noted.

It was found that on freezing the oil, a white solid precipitated out of the oil solution. A crude separation was made between the solid and oil with petroleum ether at freezing temperature. The separated yellow oil was re-examined in infrared light, and the spectrum was found to retain all the carbonyl bands. However, a few bands in the fingerprint area were lost.

Special measurements of the separated oil were obtained with a Beckman DK-2 recording spectrophotometer. The visible spectrum showed only that absorption pattern characteristic of brownish-yellow absorption. No information could be obtained from the ultraviolet spectrum, because of the strong fluorescence it exhibited in ultraviolet light. It was subsequently found that the fluorescence was due to the white solid remaining in the oil.

Carbonyl determination of the oil

A total carbonyl analysis was made on the oil in the manner described for the low boiling fraction of mango essence. A positive reading was recorded which corresponded to 8700 p.p.m. acetaldehyde in the oil.

The 2,4-DNPH's formed by reacting the oil with 2,4-dinitrophenylhydrazine (1) were chromatographed on both paper and column. On bentonite and kieselghur a number of diffuse bands were recognized. One of them was easily eluted with chloroform, but could not be crystallized. It had the fragrant aroma of mango. The rest of the hydrazones were eluted with a 1 part per 19 parts mixture of ethanol in chloroform.

On paper, the chloroform eluate chromatographed quite rapidly just behind the solvent front. The method of Gordon, Wopat, and Bernham (4) of column chromatographing high-molecular-weight hydrazones was used to purify the chloroform eluate. However, the chromatographed material could not be crystallized.

The ethanol-chloroform eluate was reduced to small volume and chromatographed on a rapid-flow 1 to 4 parts by weight bentonite-kieselghur column. Three bands traveled down when eluted with the mixture of ethanol and chloroform. The first two were not clearly resolved and no attempt was made to take the melting points of each fraction. Both bands were paper-chromatographed (10, 11). The first band was not identified but appeared to be a carbonyl of larger molecular weight than acetone. The second band was identified as that of acetaldehyde-2,4-DNPH. The third band was due to 2, 4-dinitrophenylhydrazine.

Examination of the white solid

The white solid which was crudely separated from the mango oil had a melting point of 42°-45° C. It fluoresced strongly in ultraviolet light. The solid was scanned in infrared light, but there was not enough of the material for absorption to take place.

GUAVA ESSENCE

A limited study was made of the volatile substance recovered from guava. A total of 102.7 kg. of guava puree was diluted with six times its weight of water and steam-distilled. An oil-water distillate was collected, and the two fractions were separated with petroleum ether. The recovery of guava oil was quite high compared to that of mango. Approximately 5 gm. of oil was collected and represented a concentration of 49 p.p.m. in the fruit. The aqueous phase represented a 63-fold concentration by weight of the original guava puree. The high yield of oil compared favorably to those of citrus fruits.

A gas chromatogram of the oil showed that it was a mixture of compounds. However, the resolution on the silicone column at 184° C. and 42 cm. pressure was not sharp. A total carbonyl analysis for both oil and aqueous phases was made in the manner described for mango. The readings were 9800 and 27 p.p.m. acetaldehyde, respectively. The high carbonyl reading for the oil is surprising in view of the fact that no absorption band was present in the C=O region of the infrared spectrum. However, a conjugated carbonyl would cause a shift of the C=O band from its usual absorption near 5.8μ to the 6μ region. One band of significance was the absorption of 6.1μ , normally given by unsaturated compounds. Other bands were also present in the fingerprint region. Unsaturation in the oil was tested chemically with both bromine and potassium permanganate. The tests were positive. The oil may be a mixture of hydrocarbons, much as citrus oils are.

SUMMARY

Mango juice was distilled and much of the essence was recovered. The distillate consisted of an oil and water mixture. Acetaldehyde and ethanol were identified in the water phase. The oil was found to deposit a white solid at freezing temperature. The separated oil gave a positive test for carbonyls, one of which was identified as acetaldehyde. Other compounds appear to be fairly high molecular weight aliphatic carbonyls. A preliminary examination of the white solid showed it to be strongly fluorescent in ultraviolet light. It appeared quite unreactive and, in view of the low melting point and paraffin-like appearance, may be a high molecular weight hydrocarbon.

An oil-water distillate was also recovered from guava puree. Oil recovery was large compared to mango. A total carbonyl analysis was made on both fractions. Unsaturation tests were positive for the oil.

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